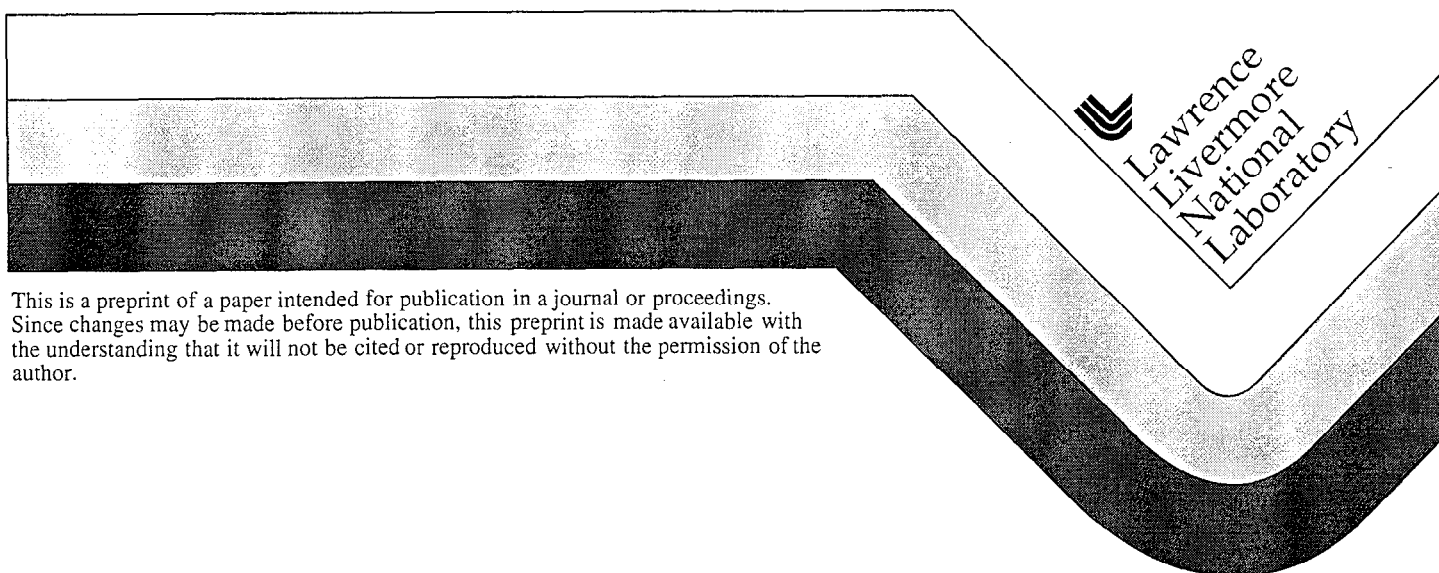# Solid Phase Microextraction Analysis of B83 SLTs and Core B Compatibility Test Units

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Solid Phase Microextraction Analysis of B83 SLTs and Core B Compatibility Test Units

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Abstract

Solid phase microextraction has permitted the efficient collection and analysis of a broad range of volatile and semivolatile compounds outgassed from materials. In 1998, we implemented a microextraction protocol at Mason and Hanger, Pantex Plant, for the analysis of weapons and compatibility test units. The chemical information that was obtained from this work is interpreted by determining the source and outgas mechanism for each compound in the weapon signature, which is a task only accomplished by analysis of material standards.

Background

Solid phase microextraction (SPME) is a new collection tool for analysis of chemicals outgassed from materials, weapons and components. Collection involves accumulating gas phase chemicals into a polymer film or composite, which is then analyzed by gas chromatography/mass spectrometry (GC/MS). The active portion of this collection device uses a 100-μm-diameter fused-silica fiber coated with an appropriate absorbent that can be up to 100-μm thick. The small size of this fiber permits direct injection into the GC and desorption at the tip of the GC column with little loss or dilution. As a result, this capability enhances handling, precision and detection especially for semivolatiles and polymer fragments and is unsurpassed by any other analytical technique.

In 1998, we implemented a new microextraction procedure for sampling weapons and compatibility test units. In that year, we sampled ten B83 weapons and three B83 Core B compatibility units. The goal of this new process is to obtain a comprehensive chemical profile by eliminating adsorption loss, which is commonly encountered in gas sampling. The only way to achieve this objective was to place the fiber in direct communication with the weapon or compatibility test unit environment.

Current applications of this work include: (1) providing integrated chemical composition of the weapon environment; (2) identifying potential material incompatibilities; (3) identifying and monitoring aging indicators, which pinpoint specific materials; (4) screening for "defects," such as an incompletely cured adhesive and organic residues left over from assembly or rebuild of weapon components; and (5) identifying material sources and sinks.

Interpretation of Chemical Signature Information

The strategy for interpretation of signature data involves collecting outgas information from materials and relating it to that seen in weapons, compatibility test units, and components. Materials include non-war reserve (WR) standards, unused parts, and deployed parts. By analyzing these materials, we can identify sources and sinks, synthesis by-products and aids, and formulation ingredients. From analysis of the weapon atmosphere, we can (1) characterize its composition; (2) identify deviation from baseline; and (3) detect manufacture or assembly defects. By combining materials and weapon data, we can differentiate degradation products from material by-products, identify specific material aging indicators (not just decomposition), and detect material defects.

In the B83 weapon, there are approximately 50 organic materials in the primary nuclear package and fireset with a combined weight of approximately 25 kg. The fireset, which is an unsealed unit, shares this headspace. As a result, there is a wealth of chemical information available for monitoring that can be used to pinpoint the condition of specific materials. We are currently monitoring 54 compounds in both the weapon and Core B compatibility test unit. The compatibility test units are helpful in verifying what we see in the weapon.

Among the more interesting findings in the analysis of materials has been the capture and detection of organics trapped within the crystalline structure of high explosives (HE). For example, we found large amounts of toluene in LX-17-1 (92.5% 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 7.5% KelF-800 polymer binder) approaching low percent. Toluene is a solvent used in the synthesis of TATB and remains trapped within its crystalline structure. In the study shown in Fig. 1, we found that heating alone does not effectively liberate toluene unless there is a previous history of stress loading. In one experiment, we sonicated a molding powder for 2 hours and found a 500-fold increase in toluene outgas level. These results call our attention to contaminants that can be trapped within crystalline HE materials and any effect they may have on the polymer binder and performance.

In the B83 weapon, LX-17-1 is the primary source of toluene and can be monitored to describe chemistry and stress loading history. Fig. 2 shows a comparison of toluene response from ten B83 weapons normalized with respect to m- and p-xylene. The relative standard deviation for toluene of 67.8% was much greater than that of the other xylene isomers, which may suggest different stress loading or shock environments for the weapons. The greater o-xylene deviation was likely the result of coelution with nonane.

Material analysis can also be used to distinguish synthesis or formulation by-products from degradation products. The most common degradation products we find in the B83 result from a back biting mechanism of polysulfide and the siloxanes. From polysulfide, we see the formation of 1,3,6,7-dioxadithionane, which is likely catalyzed by the presence of residual lead left over from the material synthesis. Although this compound contains sulfur, it is believed to be relatively benign because no corrosion of exposed copper cabling or contacts is currently seen.

Although the siloxanes are end blocked to prevent back biting, it is not possible to block all terminations. Cyclic siloxanes are formed by this degradation mechanism, however, these are difficult to distinguish from synthesis precursors and by-products. We also see relatively high

levels of linear siloxanes that are not seen at significant levels in the material standards. These compounds are believed to be a by-product of silanol condensation of end blocker fragments. This degradation reaction is important to modelers and material specialists because silanol compounds and water are formed as by-products.
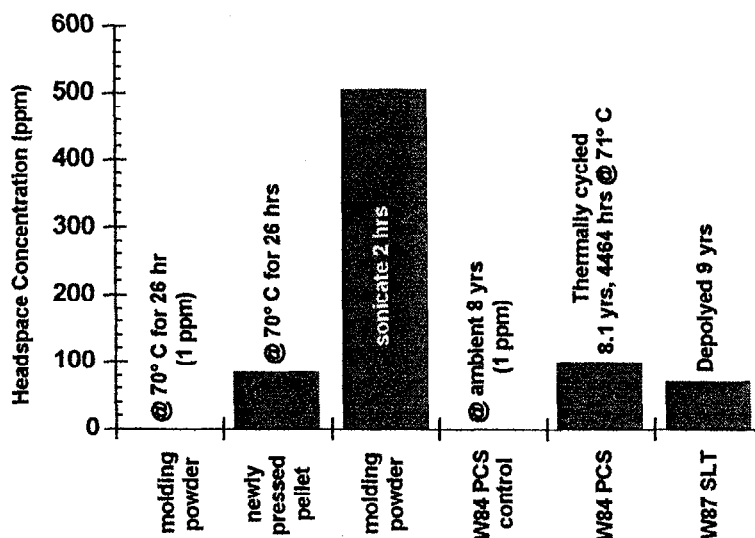
Figure 1. Comparison of toluene outgas response from non-WR and deployed LX-17-1. High toluene levels result from fracturing of TATB crystalline structure that can be induced in the laboratory by sonication or in the weapon by stress loading.
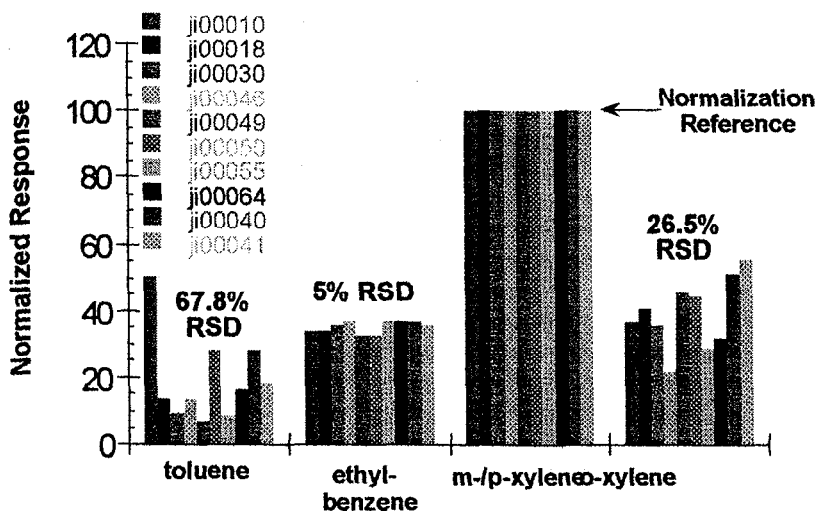
Figure 2. Analysis of ten B83 units show statistically significant variation in toluene levels that we believe reflect stress loading or shock environment of the weapon HE.

Conclusion

SPME is a new collection tool that provides chemical outgas data on materials, weapons, and components. In 1998, we were able to sample a number of B83 weapons and compatibility test units at Mason & Hanger, Pantex Plant. The strategy for interpretation requires a comparison of this data with materials outgas information. Of the more interesting findings in the analysis of materials has been the capture and detection of organics that are trapped within the crystalline structure of high explosives. In the B83 weapon, LX-17-1 is the primary source of toluene, and we believe it can be monitored to describe the chemistry and stress loading history of the HE. Material analysis can also be used to distinguish synthesis or formulation by-products from degradation products found in the weapon.